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Stoichiometric and Metal-Deficient Copper(II) Complexes of a Dinucleating Macrocyclic Ligand. Structural Studies

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Introduction

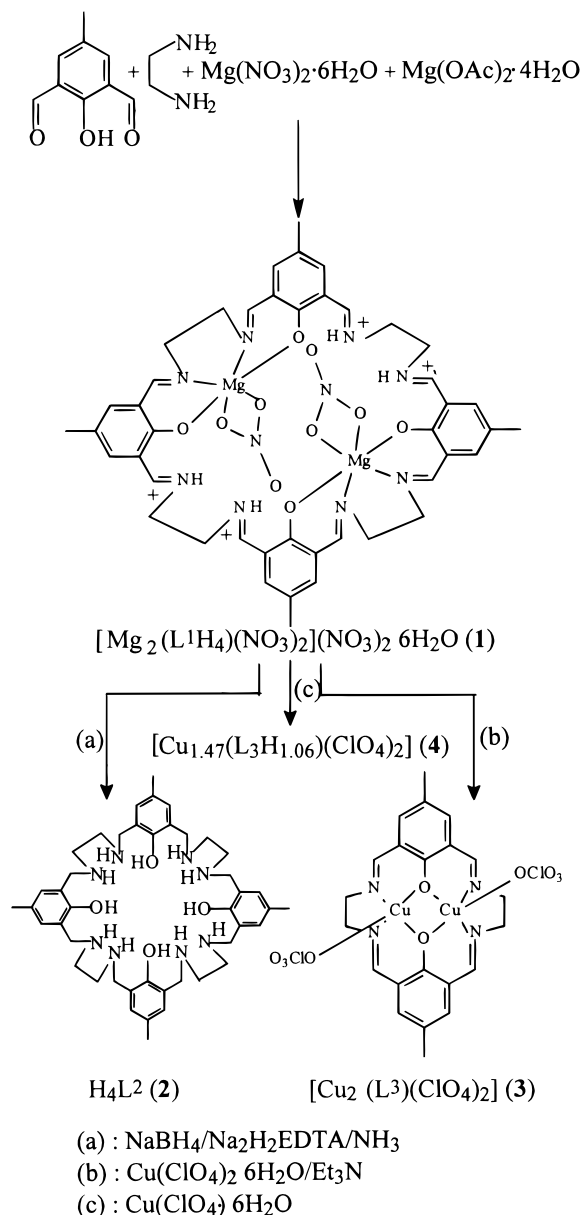
In a recent publication we have reported¹ the formation of a protonated macrocyclic magnesium compound of composition $[\text{Mg}_2(\text{L}^1\text{H}_4)(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (**1**) (shown in Scheme 1) by a template reaction involving 4-methyl-2,6-diformylphenol, 1,2-diaminoethane, magnesium acetate, and magnesium nitrate. Compound **1** on reduction and demetalation affords the 36-membered octaaminotetraphenol macrocyclic ligand H_4L^2 (**2**) which, in turn, produces a number of tetranuclear as well as trinuclear nickel(II) and copper(II) complexes. Several of these complexes have been structurally characterized^{1–3} and spin exchange interactions exhibited by the tetrameric species have been studied.¹ The transmetalation reaction of **1** with copper(II) perchlorate in the presence of triethylamine has turned out to be interesting because the product is not the expected tetranuclear copper(II) complex but a dinuclear copper(II) complex of composition $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (**3**).¹ The structure of **3**, as reported here, reveals that the ligand H_2L^3 is the [2+2] cyclized derivative of 4-methyl-2,6-diformylphenol and 1,2-diaminoethane. We also report here that the reaction between **1** and copper(II) perchlorate in absence of triethylamine is even more interesting. The product obtained in this case is an unusual copper-deficient species whose composition on the basis of the structure determination has turned out to be $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ (**4**).

Experimental Section

$[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (**3**). The method given below is a modification of the earlier reported procedure.¹

A mixture of **1** (0.58 g, 0.5 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.74 g, 2 mmol), and triethylamine (0.20 g, 2 mmol) in methanol (50 mL) was stirred at room temperature for 2 h, and the chocolate-brown product that formed was filtered. It was then dissolved in minimum volume of hot (ca. 90 °C) *N,N*-dimethylformamide (DMF) by adding the solid in portions. The DMF solution was filtered and to the filtrate was

Scheme 1



added slowly a large volume of methanol (ca. 6-fold) till incipient crystallization took place. After standing for 2 h the dark-chocolate-colored crystals that deposited were collected by filtration. The compound was then recrystallized from hot water; yield 0.56 g (80%). Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_{10}\text{Cl}_2\text{Cu}_2$: C, 37.71; H, 3.14; N, 8.00; Cu, 18.15. Found: C, 37.80; H, 3.18; N, 7.94; Cu, 18.06.

$[\text{Cu}_{2-x}(\text{L}^3\text{H}_x)(\text{ClO}_4)_2]$ ($x \approx 0.55-0.50$) (**4**). A mixture of **1** (0.58 g, 0.5 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.74 g, 2 mmol) in methanol (50 mL) was refluxed for 2 h. The dark brown product that formed was filtered off. This was recrystallized twice from a DMF–MeOH mixture in the same way as described above; yield 0.41 g (60%). Anal. Calcd for $\text{C}_{22}\text{H}_{23.1}\text{N}_4\text{O}_{10}\text{Cl}_2\text{Cu}_{1.45}$ ($x = 0.55$): C, 39.63; H, 3.47; N, 8.41; Cu, 13.83. Calcd for $\text{C}_{22}\text{H}_{23}\text{N}_4\text{O}_{10}\text{Cl}_2\text{Cu}_{1.5}$ ($x = 0.50$): C, 39.45; H, 3.43; N, 8.37; Cu, 14.24. Found: C, 39.56; H, 3.41; N, 8.40; Cu, 14.04.

Safety Note. Perchlorate salts are potentially explosive and should

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(1) Mohanta, S.; Nanda, K. K.; Werner, R.; Haase, W.; Mukherjee, A.; Dutta, S. K.; Nag, K. *Inorg. Chem.* **1997**, *36*, 4656.

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Table 1. Crystallographic Data for $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (**3**) and $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ (**4**)

empirical formula	$\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_{10}\text{Cl}_2\text{Cu}_2$	$\text{C}_{22}\text{H}_{23.06}\text{N}_4\text{O}_{10}\text{Cl}_2\text{Cu}_{1.47}$
fw	700.42	667.81
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	8.290(3)	8.183(2)
<i>b</i> , Å	8.384(3)	8.334(2)
<i>c</i> , Å	9.821(4)	9.874(2)
α , deg	81.77(2)	81.31(2)
β , deg	69.36(2)	70.09(2)
γ , deg	78.97(2)	80.66(2)
Z	1	1
<i>V</i> , Å ³	624.8(4)	621.4(2)
ρ_{calcd} , gcm ⁻³	1.861	1.785
μ , mm ⁻¹	1.982	1.552
<i>T</i> , K	200(2)	203(2)
<i>R</i> 1, ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0353,	0.0345
w <i>R</i> 2 (all data)	0.0991	0.0875

$$^a R1 = [\sum ||F_o| - |F_c|| / \sum |F_o|]. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

be handled small quantities. No problems were encountered with the complexes reported in this study, however.

Determination of the Crystal Structures of $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (3**) and $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ (**4**).** Crystals suitable for the structure determinations of **3** and **4** were obtained by diffusing methanol to the DMF solutions of the corresponding compounds.

Diffraction data were collected at 200–203 K on a Siemens R3m/V diffractometer in the ω - 2θ scan mode using graphite-monochromated Mo K α radiation. Three standard reflections were periodically monitored and in both the cases no crystal decay was observed. The intensity data were corrected for Lorentz and polarization effects and semiempirical absorption correction was made from Ψ scans. Pertinent crystallographic data are given in Table 1. In the case of **3** a total of 2977 reflections were collected, of which 2817 reflections were considered unique ($R_{\text{int}} = 0.0404$) and used for structure determination. The corresponding reflections used for **4** were 2877 and 2719 ($R_{\text{int}} = 0.0232$).

The structures were solved by direct and Fourier methods and refined by full-matrix least-squares methods based on F^2 using the programs SHELXTL-PLUS⁴ and SHELXL-93.⁵ Neutral atom scattering factors were taken from Cromer and Waber.⁶

All non-hydrogen atoms were refined anisotropically. For **3**, hydrogen atom positions were roughly observed in difference Fourier map. They were then placed at idealized positions and refined with a riding model. The final least-squares refinement ($I > 2\sigma(I)$) converged to $R = 0.035$ and w*R*2 (for all data) = 0.095. In the final difference Fourier map the maximum and minimum peaks correspond to 0.611 and $-0.791 \text{ e } \text{\AA}^{-3}$, respectively.

In the case of **4**, during the course of refinement it became apparent that in the asymmetric unit the metal site is not fully occupied, albeit full occupancy was observed for the chlorine position of the perchlorate anion. Refinement led to a ratio of 0.73:1 for Cu/Cl, which is in excellent agreement with the ratio obtained from energy dispersive spectroscopic and chemical analyses. Thus, on the basis of the X-ray analysis **4** is formulated as $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$. The perchlorate anion is disordered over two sites with common Cl and O(11) positions and site occupation factors for the other oxygen atoms are 0.54 [for 0(12)–0(14)] and 0.46 [for 0(122)–0(142)]. The refinement converged to R ($I > 2\sigma(I)$) = 0.034 and w*R*2 (all data) = 0.087, and final difference Fourier map peaks were 0.297 and $-0.462 \text{ e } \text{\AA}^{-3}$.

Analyses. Energy dispersive spectroscopic analysis was carried out on a JSM-5400 electron microscope. Quantitative electron microprobe analysis was performed on polished crystals inserted into an epoxy matrix. Six measurements on different crystals were made. Elemental

(C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. Copper was estimated gravimetrically with α -benzoin oxime.⁷

Results and Discussion

Synthesis and Characterization. Despite the fact that the magnesium compound $[\text{Mg}_2(\text{L}^1\text{H}_4)(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (**1**) is readily obtained by the metal template reaction, the macrocyclic ligand H_4L^1 could not be isolated in the metal-free state. Demetalation of **1** presumably leads to hydrolytic cleavage of the imino moieties of the macrocyclic ligand. To prepare a tetranuclear copper(II) complex of H_4L^1 , transmetalation reaction of the magnesium complex (**1**) (shown in Scheme 1) was considered to be an obvious choice. However, when **1** (1 equiv) is reacted with copper(II) perchlorate (4 equiv) and triethylamine (4 equiv) the product obtained is the dinuclear complex $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (**3**) whose characterization data have already been reported.¹ The formation of **3** indicates that the replacement of magnesium by copper induces the nucleophilic attack of water on a pair of diagonally opposite protonated imines of **1** into two identical fragments, which then undergoes deprotonation, additional copper binding, and amine–aldehyde condensation. In contrast to the present case where a [4+4] macrocyclic compound is transformed to a [2+2] system, there is a reported case⁸ for a [2+2] \rightarrow [4+4] macrocyclic rearrangement that has been implicated due to transamination reactions.

Interestingly, when the above transmetalation reaction is carried out in the absence of triethylamine the product is found to be a copper-deficient species with the composition $[\text{Cu}_{2-x}(\text{L}^3\text{H}_{2x})(\text{ClO}_4)_2]$ ($x \approx 0.55$ – 0.50) (**4**). In fact repeated syntheses of the metal-deficient complex yields the same composition each time. Initially, it was thought to be a cocrystallized product of $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ and $[\text{CuMg}(\text{L}^3)(\text{ClO}_4)_2]$ compounds. However, energy dispersive spectroscopic analysis of the single crystals of **4** has established the absence of magnesium or any other metallic impurity. Indeed, the Cu/Cl ratio 0.72(3):1.00(3) determined by quantitative electron microprobe analysis is in very good agreement with the composition $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ obtained from the X-ray structure determination (see later). Attempts to convert the nonstoichiometric complex (**4**) to the stoichiometric complex (**3**) by treating **4** with the required amounts of copper(II) perchlorate and triethylamine were not met with success. However, when **4** is boiled with water, a part of it goes into solution and the filtrate, on concentration, affords **3**.

Description of the Structures of $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (3**) and $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ (**4**).** The structure of **3** is illustrated in Figure 1 along with the atom labels. Atomic coordinates and selected bond distances and angles are given in Tables 2 and 3, respectively. The compound has a centrosymmetric structure with the center of inversion at the middle of the Cu_2O_2 plane. The two square pyramidal copper centers are bridged by the two phenoxide oxygen atoms, and the CuN_2O_2 plane is completed by the two imine nitrogens. The perchlorate ions are transaxially bound above and below the dinuclear centers. The macrocyclic ligand adopts roughly a planar structure in which the two phenyl rings are parallel.

The final atomic coordinates of **4** are given in Table 4, while the selected bond distances and angles are summarized in Table 3. The cell parameters of **4** (Table 1) show small but significant differences from those of **3**. As expected, the cell volume of **3**

(4) SHELXTL-PLUS; Siemens Crystallographic Research Systems; Madison, WI, 1990.

(5) Sheldrick, G. M. SHELXL-93: A Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1993.

(6) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(7) Vogel, A. I. *A Textbook of Quantitative Inorganic Analysis*, 3rd ed.; Longmans: London, 1961.

(8) Brooker, S.; McKee, V.; Shepard, W. R.; Pannell, L. K. *J. Chem. Soc., Dalton. Trans.* **1987**, 2555.

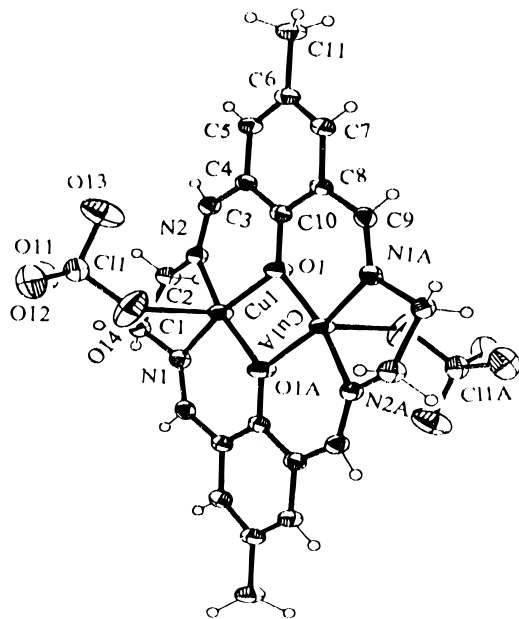


Figure 1. ORTEP representation of the molecular structure of $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (**3**) showing the 50% probability of thermal ellipsoids.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) of $[\text{Cu}_2\text{L}^3(\text{ClO}_4)_2]$ (**3**)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Cu(1)	4184(1)	4372(1)	6495(1)	24(1)
O(1)	3565(2)	5611(3)	4928(2)	31(1)
N(1)	4983(3)	2832(3)	7810(2)	22(1)
N(2)	1843(3)	4185(3)	7645(2)	22(1)
C(1)	3516(3)	2644(3)	9184(3)	23(1)
C(2)	1804(3)	2882(3)	8837(3)	26(1)
C(3)	491(3)	4989(3)	7375(3)	23(1)
C(4)	508(3)	6183(3)	6116(3)	22(1)
C(5)	-1101(3)	7063(3)	6073(3)	24(1)
C(6)	-1233(3)	8193(3)	4915(3)	25(1)
C(7)	279(3)	8429(3)	3762(3)	24(1)
C(8)	1932(3)	7572(3)	3721(3)	21(1)
C(9)	3435(3)	7877(3)	2418(3)	22(1)
C(10)	2036(3)	6442(3)	4925(3)	22(1)
C(11)	-2986(3)	9120(4)	4907(3)	32(1)
Cl(1)	3166(1)	7641(1)	8631(1)	27(1)
O(11)	2680(3)	6619(3)	9970(2)	44(1)
O(12)	3932(4)	8955(3)	8804(3)	45(1)
O(13)	1665(4)	8229(4)	8201(3)	58(1)
O(14)	4456(4)	6690(3)	7520(3)	59(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(624.8(4) \AA^3) is larger relative to that of **4** (621.4(2) \AA^3) in which the metal site is 73.3% occupied. The presence of a crystallographic inversion center in **4** indicates that the copper is statistically distributed over the two equivalent positions. Unlike **3**, the perchlorate ion in the asymmetric unit of **4** is disordered over two sites having common Cl and O(11) positions and is modeled, as shown, in Figure 2.

The metrical parameters given in Table 3 for complexes **3** and **4** show small differences in the metal coordination spheres. In **3** the in-plane Cu–N(1), Cu–N(2), Cu–O(1'), and Cu–O(1') bond distances range from 1.890(2) to 1.898(2) \AA , while the axial Cu–O (perchlorate) bond (2.394(3) \AA) is considerably elongated due to the Jahn–Teller effect of copper(II). The metal center is displaced from the basal least-squares plane toward O(14) by 0.156(1) \AA . The Cu...Cu separation is 2.901(1) \AA with the intervening Cu–O(1)–Cu' angle of 99.70(9)°. On the other hand, the in-plane metal–ligand distances in **4** vary

Table 3. Selected Bond Distances (\AA) and Angles (deg) of $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$ (**3**) and $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ (**4**)

	3	4
Cu–N(1)	1.890(2)	1.896(2)
Cu–N(2)	1.894(2)	1.902(2)
Cu–O(1)	1.898(2)	1.880(2)
Cu–O(1)	1.898(2)	1.870(2)
Cu–O(14)	2.394(3)	2.45(2)
Cu–O(142)		2.37(2)
O(1)–C(10)	1.326(3)	1.316(3)
N(1)–C(9)	1.286(3)	1.286(3)
N(2)–C(3)	1.285(3)	1.282(3)
N(1)–C(1)	1.477(3)	1.468(3)
N(2)–C(2)	1.479(3)	1.478(3)
Cu...Cu'	2.9013(13)	2.7915(10)
N(1)–Cu–N(2)	90.36(9)	90.88(8)
N(2)–Cu–O(1)	93.60(9)	91.36(8)
N(1)–Cu–O(1')	94.18(9)	92.42(8)
O(1)–Cu–O(1)	80.30(9)	83.82(8)
N(1)–Cu–O(14)	94.51(11)	90.7(5)
N(2)–Cu–O(14)	98.14(9)	96.7(4)
O(1')–Cu–O(14)	91.26(9)	92.4(4)
O(1)–Cu–O(14)	94.74(11)	99.0(5)
N(1)–Cu–O(1)	169.32(9)	169.69(8)
N(2)–Cu–O(1')	169.22(9)	170.26(9)
Cu–O(1)–Cu'	99.70(9)	96.18(8)

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Cu(1) ^b	4215(1)	4388(1)	6435(10)	25(1)
O(1)	3527(2)	5566(2)	4898(2)	35(1)
N(1)	5022(2)	2882(2)	7778(2)	24(1)
N(2)	1849(2)	4147(2)	7560(2)	28(1)
C(1)	3539(3)	2715(3)	9121(2)	27(1)
C(2)	1841(3)	2843(3)	8756(3)	31(1)
C(3)	479(3)	4992(3)	7361(2)	24(1)
C(4)	485(3)	6181(3)	6113(2)	22(1)
C(5)	-1105(3)	7087(3)	6070(2)	25(1)
C(6)	-1235(3)	8221(3)	4918(3)	25(1)
C(7)	285(3)	8452(3)	3758(2)	25(1)
C(8)	1921(3)	7571(3)	3712(2)	22(1)
C(9)	3425(3)	7868(3)	2424(2)	23(1)
C(10)	2024(3)	6422(3)	4905(2)	22(1)
C(11)	-2973(3)	9149(3)	4910(3)	35(1)
Cl(1)	3166(1)	7658(1)	8647(1)	30(1)
O(11)	2693(3)	6625(2)	9991(2)	45(1)
O(12) ^c	1688(19)	8153(23)	8181(19)	54(3)
O(13) ^c	3902(29)	9031(20)	8778(24)	43(3)
O(14) ^c	4491(22)	6691(24)	7591(18)	47(3)
O(122) ^d	1569(23)	8423(51)	8398(40)	64(5)
O(132) ^d	4107(49)	8901(34)	8790(25)	47(5)
O(142) ^d	4199(58)	6779(31)	7471(25)	65(6)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b Occupancy factor 0.733(2). ^c Occupancy factor 0.54(9). ^d Occupancy factor 0.46(9).

between 1.870(2) and 1.902(2) \AA , while the average Cu–O (perchlorate) distance is 2.41(4) \AA . Significantly, the Cu...Cu separation in **4** (2.791(1) \AA) is shorter relative to that of **3** (2.901(1) \AA), underscoring the effect of partial occupancy of the metal sites. For the same pair of bonds the difference between the bond distances of **3** and **4** varies from 0.006 to 0.028 \AA , while for the same pair of angles the difference ranges from 0.5 to 3.5°.

The structure of **3** may be compared with those of the related propylene-bridged macrocyclic dicopper(II) complexes $[\text{Cu}_2(\text{L}^4\text{X}_2)]$ (X = Cl, Br, I)⁹ derived from 4-methyl-2,6-di-

(9) Mondal, S. K.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J.; Nag, K. *Inorg. Chem.* **1990**, *29*, 1325.

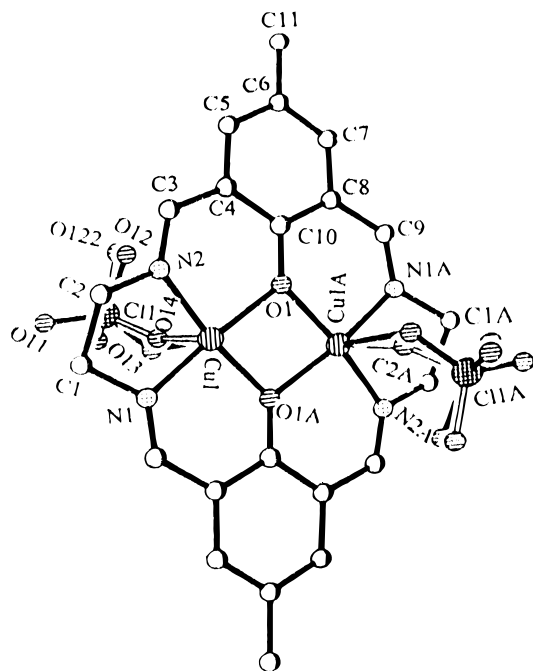


Figure 2. Perspective view of the structure of $[\text{Cu}_{1.47}(\text{L}^3\text{H}_{1.06})(\text{ClO}_4)_2]$ (**4**).

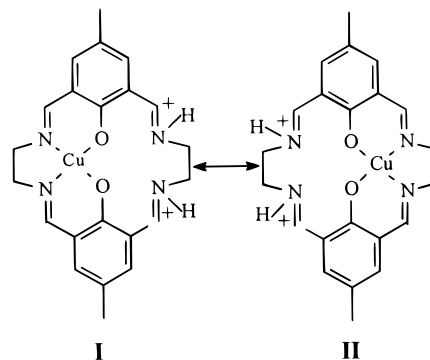
formylphenol and 1,3-diaminopropane. In these compounds the in-plane copper–ligand distances (average 1.98 Å), the $\text{Cu}\cdots\text{Cu}$ separation (average 3.13 Å), and the $\text{Cu}-\text{O}(\text{phenoxide})-\text{Cu}$ angle (average 103°) are all larger relative to those of **3** and are consistent with the larger cavity size of the macrocycle H_2L^4 . It will be more relevant to compare the structure of **3** with that of $[\text{Cu}_2(\text{L}^5)(\text{H}_2\text{O})_2](\text{BF}_4)_2$,^{10,11} obtained by the metal template reaction between 4-methyl-2,6-diacetylphenol and 1,2-diaminoethane, because both the compounds have five-membered ethylene lateral chains. The structural parameters reported^{10,11} for $[\text{Cu}_2(\text{L}^5)(\text{H}_2\text{O})_2](\text{BF}_4)_2$ have some uncertainties due to severe disordering of the fluoroborate anions. Nevertheless, the average bond distances in the basal plane ($\text{Cu}-\text{N} = 1.90$ Å; $\text{Cu}-\text{O} = 1.89$ Å), the $\text{Cu}-\text{O}(\text{phenoxide})-\text{Cu}$ bridge angle ($96.5(5)$;¹⁰ $99.2(5)^{\text{O}11}$) and the nonbonded $\text{Cu}\cdots\text{Cu}$ distance ($2.847(4)$ Å,¹⁰ $2.997(3)$ Å¹¹) of this compound are quite similar to those of **3**.

(10) Carlisle, W. D.; Fenton, D. E.; Roberts, P. B.; Casellato, U.; Vigato, P. A.; Graziani, R. *Transition Met. Chem.* **1986**, *11*, 292.

(11) Thompson, L. K.; Mondal, S. K.; Tandon, S. K.; Bridson, J.; Park, M. K. *Inorg. Chem.* **1996**, *35*, 3117.

The structural parameters of another five-membered lateral chain macrocyclic complex $[\text{Cu}_2(\text{L}^6)(\text{DMF})_2](\text{ClO}_4)_2$,¹² obtained by reacting 4-*tert*-butyl-2,6-diformylphenol, 1,2-diaminobenzene, and copper(II) perchlorate (1:1:1), compare very well with those of **3**. In this case $\text{Cu}-\text{N} = 1.896(9)$ Å, $\text{Cu}-\text{O} = 1.899(8)$ Å, $\text{Cu}\cdots\text{Cu} = 2.929(4)$ Å, and $\text{Cu}-\text{O}(\text{phenoxide})-\text{Cu} = 100.9(3)^\circ$.

It is relevant at this stage to comment on the composition of complex **4**. The metal deficiency in this compound seems to arise due to statistical distribution of the two resonating forms **I** and **II** of the diprotonated mononuclear macrocyclic complex



$[\text{Cu}(\text{L}^3\text{H}_2)(\text{ClO}_4)](\text{ClO}_4)$ and the dinuclear complex $[\text{Cu}_2(\text{L}^3)(\text{ClO}_4)_2]$, approximately in the ratio 1:1 in the crystal lattice. The fact that **3** can be isolated by boiling **4** with water provides support to this view.

In conclusion, two unusual observations have emerged out of this study. First, the transformation of the [4+4] macrocyclic ligand (H_4L^1) to its [2+2] replica (H_2L^3) during the transmetalation reaction. Second, the unprecedented synthesis of the metal-deficient macrocyclic complex **4**. It is worth mentioning that the first synthesis of **3** involving a sequential route was reported¹³ some 25 years ago.

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Supporting Information Available: Tables of crystal data and structure refinement, anisotropic thermal parameters, complete bond lengths and angles, and hydrogen atom coordinates for **3** and **4** (7 pages). Ordering information is given on any current masthead page.

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